N67-30817

MATERIALS TECHNOLOGY REPORT

CONTRACT NAS 4-1009

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FOREWORD

This report summarizes the materials selected and tests that have been performed on Contract NAS 4-1009. The information and data presented have been removed in part from the monthly progress reports and test reports that have been submitted throughout the course of the program. All detail data are referenced to reports and test specifications submitted during the program. A number and title listing of the reports is given in Section VIII.

I. INTRODUCTION

The program objectives were to conduct the necessary material evaluations and select the most practical elastomeric silicone base materials to provide a thermal protection system for the Mach 8 X-15-2 airplane.

At the time of program initiation the Martin Company had developed and flight tested a sprayable, room temperature cure, elastomeric silicone ablative material, designated MA-25S. Program requirements were to refine the application techniques, perform necessary material property and thermal performance tests and derive the system design. Necessarily other materials were required for protection of leading edges, antennas, hard point or bearing locations, etc., on the airplane. Therefore, material selection tests were conducted for these specific areas to complete the design.

This report serves as a summary of the materials selected, tasks performed, and typical results obtained for the design of the thermal protection system for the Mach 8, X-15-2 airplane.

II. MATERIALS SELECTION

This section provides a list of the materials selected for the thermal protection system, their application and a brief description of the material and origin.

A. Primary Heat Shield Material

A proprietary material, MA-25S, developed by the Martin Company was selected as the primary ablative material which was to be employed over the greater portion of the X-15-2 structure. This material is a sprayable, room temperate curing elastomeric silicone base material. The base material consists of a vinyl curing methyl-phenyl polysiloxane polymer. The base resin is compounded with various filler materials to improve ablative performance and suitable solvents to control cure rate and lower viscosity for spray application. When properly processed the material can be applied utilizing conventional spray type equipment.

B. Leading Edge Materials

The leading edge material selected, ESA-3560 II-A, was primarily developed for the Martin PRIME Lifting Body Program. Previous applications of this material used a honeycomb core reinforcement which could not be adapted to the small radii leading edges of the X-15-2. Therefore, the basic formulation was slightly modified by compounding silica fibers into the material to provide reinforcement in lieu of the honeycomb. Ground and flight tests on the X-15-2 verified the selection of the ESA-3560 II-A material for leading edge applications.

This material consists of an elevated temperature vinyl curing methyl-phenyl polysiloxane resin with appropriate fillers and reinforcing media for compression molding to leading edge configurations.

C. Adhesive and Hard Point Material

The Dow Corning DC 93-027 room temperature curing silicone elastomer was chosen as the leading edge adhesive and trowelable material for hard point applications. Certain locations on the airplane were subject to bearing loads which the MA-25S material could not withstand without mechanical degradation. Therefore, there was a need for a modified ablator for these limited areas. Rather than modifying or developing an efficient ablative material for these locations, a commercially available material was selected for use. During the course of the hard point material selection tests the DC 93-027 was determined to be a good adhesive and was ultimately selected for the leading edge bond material.

The DC 93-027 is commercially available from Dow Corning Aerospace Materials Division.

D. Top Coat Material

The DC 90-090 sprayable, silicone sealant was selected as the top coat material. During the program development it was determined that the ablative materials employed required an overcoat or wear layer to minimize abrasion. This material when applied in a continuous film imparts impact resistance (to liquid oxygen) and seals the surface to possible fluid absorption in addition to improving surface abrasion resistance.

The titanium dioxide pigmented silicone sealant DC 90-090 is commercially available from Dow Corning Aerospace Materials Division.

III. APPLICATION PROCESS DEVELOPMENT -- MA-25S

A preliminary application process for large scale equipment was initially defined and large inconel sheets were sprayed in vertical positions to verify the thickness control, density, cure time, hardness and general properties of the MA-25S material. At this stage the MA-25S compatibility, mechanical, thermal and ablation test models were fabricated by this process to meet the requirements of the respective test specifications XR-1, XR-2, XR-3 and XR-4.

Additional process evaluations were conducted when it was determined that some blisters and slight delaminations in the MA-25S material had been noted after the first flight test on the X-15-2 aircraft. To remedy this condition a program was initiated to evaluate various spray coating techniques. Test panels were prepared and tested in the Martin Radiant Heat Facility.

Nine panels were sprayed with the following variations in spray procedures:

TABLE 1

Panel No.	Application Method
1	Sprayed to 0.125 thickness with approximately 5 minutes between spray coats.
2	Sprayed 0.062 inches thick and cured 16 hours. Sprayed with heptane until wet then an additional 0.063 in. thickness of MA-25S was applied.

TABLE 1 (Cont'd)

Panel No.	Application Method
3	Sprayed 0.062 inch thick and cured 16 hours. The MA-25S surface was sanded with No. 60 grit sandpaper and an additional 0.063 coating of MA-25S was applied.
4	Sprayed 0.062 inches thick and cured 16 hours. A coating of clear silicone resins thinned with heptane was applied and allowed to dry 5 minutes. An additional 0.063 inch thick coating of MA-25S was applied.
5	Sprayed 0.062 inches thick and cured 16 hours. The MA-25S surface was coated with A1200 primer, allowed to dry one hour then 0.063 inches of MA-25S was applied.
6	Sprayed 0.062 inches thick and cured 16 hours. Sprayed an additional 0.063 inches of MA-25S with no treatment or sanding of the cured material.
7	Sprayed 0.125 inches of MA-25S and cured for 16 hours, followed by another 0.125 thickness of MA-25S.
8.	Sprayed 0.060 inches of MA-25S and cured 16 hours followed by another 0.190 thickness of MA-25S.
9	Same as Panel 8 except the panel was sprayed with white silicone paint after the MA-25S had cured.

MA-25S was applied to Panel 1 by spraying continuous coats, allowing time for the solvent to flash off between coats. Panels 2 through 9, except Panel 8, were sprayed to approximately one-half the final thickness, cured 16 hours, then the MA-25S surface was treated as indicated in Table 1 prior to completion of the MA-25S application.

Panels 2 through 6 had 0.125 inches of MA-25S and Panels 7 through 9 had 0.250 inches of MA-25S.

The panels were tested in the Martin Radiant Heat Facility by heating the MA-25S surface to a temperature of approximately 1600°F and holding this face temperature until the back face of the metal substrate reached 600°F. Following the tests the panels were sectioned and examined for blisters and delaminations.

All of the panels had characteristic surface cracks leading down to the virgin material. However, these cracks varied in size, the extent of the cracking being a function of the residual solvent content of the MA-25S material. The panels with no surface treatment between coats (Panels 1 and 6) were the best of the group having a minimum of surface cracks and no delaminations or blisters. Panel 3 which was sanded, did not show the degree of delamination in the Radiant Heat Test as had been observed in the Plasma Arc Test. However, observation of the panel while the test was in progress indicated that there was a greater amount of solvents in this panel than in Panels 1 and 6. The panels which were sprayed with heptane and heptane thinned silicone resin (Panels 2 and 4) blistered and the char layer delaminated and became completely detached during the test. Panel 5, which was sprayed with A-1200 silicone primer, had separation of the char at the primer layer.

Panels 7 and 8 had larger cracks and deeper char than Panel 1 through 6 due to the greater thickness of MA-25S and the longer time required to reach the back face temperature of 600°F. There was no blistering or char delamination in these panels. Panel 9 had two coats of white silicone paint sprayed on the MA-25S surface. The second coat of silicone paint blistered and peeled off during the test but the first coat remained in place until the heat became intense enough to ignite the MA-25S material.

These tests indicate that the best spray technique is one in which solvent absorption and porous layers can be excluded from the Ablative system. This can best be accomplished by either a continuous spray operation or by a step operation where a given thickness is applied, allowed to cure, then the application continued without surface treatment of the cured material. No evidence of laminations were observed when this technique was used. These conclusions were arrived at by examination of both radiant heat and plasma arc test specimens.

IV. COMPATIBILITY TESTING

Tests were conducted, as required, to evaluate the compatibility of the elastomeric silicone ablative materials selected with the fuels and fluids that the ablative materials will potentially come in contact with on the X-15-2 aircraft.

The compatibility tests consisted of liquid oxygen impact tests and liquid and/or vapor immersion exposures in the following fluids: water, anhydrous ammonia, hydrogen peroxide liquid and steam, liquid and gaseous oxygen, liquid and gaseous nitrogen, nonpetroleum base cronite hydraulic fluid (Standard Oil 8515), hydraulic fluid MIL-H-5606 and gaseous helium. The tests were performed in accordance with XR-1.

A. MA-25S Compatibility Test Results

The MA-25S material was determined to be compatible with the system fuels and fluids with the following two exceptions.

1. Exposure of the MA-25S material to hydraulic fluids is undesirable due to discoloration and weight gain due to absorption. However, this is not considered detrimental since the bond to metal is not impaired.
2. The MA-25S material when tested in accordance with MSFC Spec-106A, "Testing Compatibility of Materials for Liquid Oxygen Systems" was found to be impact sensitive.

B. Leading Edge Material, ESA-3560 II-A Compatibility Test Results

The ESA-3560 II-A material was found to be compatible with the system fuels and fluids with the following exception and observations.

1. The ESA-3560 II-A material was found to be LOX impact sensitive when tested in accordance with MSFC Spec-106A.

2. A color change was noted from exposure to liquid and gaseous ammonia indicative of a chemical reaction between ammonia and one of the filler materials in the ablative material. The reaction was a surface phenomenon and is not considered detrimental.

3. Exposure to hydraulic oils caused surface tackiness and a 1% weight increase due to absorption. These material changes are not considered significant.

C. Hard Point Material, DC 93-027, Compatibility Test Results

The DC 93-027 compatibility test results were essentially the same as those obtained for the MA-25S material. Hydraulic fluids caused discoloration and weight increases which were not significant. The DC 93-027 material was determined to be LOX impact sensitive.

V. LOX IMPACT TESTING

The general compatibility testing showed all the elastomeric silicone materials to be LOX impact sensitive when tested in accordance with MSFC Spec-106A at an impact level of approximately 72 ft-lb. The LOX impact sensitivity of these materials generated considerable concern about the X-15-2 aircraft safety.

The first consideration made was that since the ablative materials are an external coating, a 72 ft-lb. impact level requirement was perhaps too stringent. Additional tests were requested by NASA FRC to determine the threshold level of impact sensitivity. Due to the physical location and limited use of leading edge and hard point materials, the basic concern was placed upon the primary heat shield material, MA-25S.

Threshold impact level tests in liquid oxygen were conducted at Martin, Thiokol and the Southwest Research Institute. The test results from the three sources were essentially the same. In addition, materials that were known to be LOX compatible and that could be applied as an adherent coating over the MA-25S material were evaluated for their potential protection capability. A summary of these results were:

Material	Threshold Level	
	Ft-lb	Ft-lb/in^2
1. MA-25S	1.67	8.5
2. Top Coat Materials		
a) Vydax AR	80 (compatible)	
b) DC 90-090	80 (compatible)	
3. Top Coat Material Applied over MA-25S		
a) MA-25S/Vydax AR	3.33	17.0
b) MA-25S/DC 90-090	5.0	25.5

The DC 90-090 material, although a silicone base material, was found to be compatible. Most silicone materials are not LOX compatible. When silicone materials are compounded for ablation applications the density is lowered either by foaming or incorporation of syntactic foam fillers. The presence of these built in air pockets lower the threshold level of impact sensitivity due to adabatic compression of the entrapped air. This explains the low impact levels determined with the MA-25S and other candidate elastomeric silicone ablative materials.

Although the DC 90-090 material did not appreciably increase the threshold level of impact sensitivity, the material was selected as a top coat material because of the improved abrasion resistance it imparted to the material. A top coat was also desirable since it would limit the migration of ablator particles into compartments of the X-15-2.

Additional LOX impact testing conducted at Martin where test panels were submerged in liquid oxygen and impacted at various levels revealed that there was no audible noise and only slight panel discoloration to the approximate 30 ft-lb level. At test levels above 30 ft-lb there was an audible noise accompanied by a flash with material degradation at the impact location. The most significant result was that there was no propagation of detonation across the material. Where burning occurred, the material was not self-extinguishing until all traces of liquid had evaporated from the panel surface.

Currently, modifications are being made to the X-15-2 liquid oxygen system and contamination control procedures are being developed for the ablative material application to prevent these materials from entering areas where they could possibly come in contact with liquid oxygen.

VI. PHYSICAL PROPERTIES TESTING

Mechanical and thermal properties tests were conducted by the Materials Engineering Laboratories, Martin-Baltimore, on the primary MA-25S ablator and selected leading edge and hard point materials. All values to be reported in XR-10 were ascertained by testing in conformance to applicable test methods defined in XR-2 and XR-3.

The thermal properties data were utilized as inputs to the Martin T-CAP III charring ablation computer program. This program is used to analytically determine the thickness of materials required and expected structural temperatures for the X-15-2 design missions.

VII. PLASMA ARC THERMAL PERFORMANCE EVALUATIONS

Plasma arc materials screening tests and selected materials performance tests were conducted in the Martin Company, 1 MW F-5000 Plasma Arc test facility.

Candidate leading edge and hard point materials were evaluated at simulated heating rate and enthalpy conditions characteristic of the environment expected on the X-15-2 airplane. Heating rates of 140 and 47 Btu/ft^2-sec at enthalpy levels of 1300 and 600 Btu/lb were selected for leading edge screening tests. Hard point material screening tests were performed at heating rates of 15 and 2 Btu/ft^2-sec and an enthalpy level of 600 Btu/lb. Materials were selected on the basis of their thermal ablation performance and the actual results are documented in XR-14.

Ablation performance tests were conducted on various thicknesses of the MA-25S material at heating rates from 2 to 15 Btu/ft^2-sec to yield back face temperatures of 600°F and 800°F at test completion. These data were determined to permit correlation of the thermal properties and ablation model utilized in the Martin T-CAP III charring ablation computer program. Development of an analytical procedure to describe the thermal ablation performance of a material is important to design the thermal protection system. Results of this testing are documented in XR-15.

VIII. SUMMARY OF TEST SPECIFICATIONS AND TEST REPORTS

XR-1, Heat Shield Materials Compatibility Tests

XR-2, Heat Shield Materials Mechanical Property Tests

XR-3, Heat Shield Materials Thermal Property Tests

XR-4, MA-25S Ablation Properties Test Plan

XR-5, MA-25S Process Tolerance Test Plan

XR-6, Leading Edge & Hard Point Materials Screening Test Plan

XR-7, Flight Test Plan - First Flight

XR-8, Leading Edge & Hard Point Materials Requirements

XR-9, Antenna Protection Test Plan

XR-10, Materials Design Data Book (to be published)

XR-11, Leading Edge & Hard Point Material Ablation Properties Test Plan

XR-12, Heat Shield Design Approaches for Special Areas

XR-12A, XR-12B, Revised XR-12

XR-13, Flight Test Plan - Second Flight

XR-14, Leading Edge & Hard Point Screening Test Report

XR-15, MA-25S Ablation Properties Test Report

XR-16, General Compatibility Tests

XR-17, L.O.X. Impact Test Plan

XR-18, Leading Edge & Hard Point Materials Ablation Properties Test Report

XR-19, Ablator Contamination Protection Plan

XR-20, Demonstration Plan - Contamination Control

XR-21, Flight Test Plan - Third Flight